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(54) GRAPHITE CRUCIBLE FOR PRODUCING SILICON SINGLE CRYSTAL

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a graphite crucible little in its breakage, etc., on a silicon single crystal-pulling operation, etc., and excellent in durability by controlling production conditions so that an elasticity, an average pore diameter and an opened pore rate measured by a method of mercury penetration are specific values, respectively.
SOLUTION: This graphite crucible is produced by controlling the particle size of coke powder used as a raw material for producing the graphite crucible to a prescribed range, optimizing conditions for heating and kneading the coke powder with a binder, such as a binder additive rate, and further controlling the temperature of graphitization to a range of 2000-3000°C. Thus, the graphite crucible used for producing a silicon single crystal and having characteristics consisting of an elasticity of 800-1600kg/mm2, an opened pore rate of 10-20%, and an average pore diameter (d) of 3-7μm measured by a method of mercury penetration is obtained. When a silicon single crystal is pulled up by Czochralski method, a quartz crucible for melting silicon is held with the graphite crucible from outside and pulled up. A strain generated in the graphite crucible can thereby be reduced.

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CLAIMS

[Claim(s)]
[Claim 1] The average pore diameter d measured by the method of mercury penetration is 3 micrometer<d <=7micrometer, and the rate of an open pore is 10 - 20%, and an elastic modulus is 2 800-1600kg/mm. Graphite crucible for silicon single crystal manufacture characterized by having the property.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the graphite crucible used for raising actuation of the silicon single crystal by the Czochrlski method (it is hereafter written as a "CZ process").

[0002]
[Description of the Prior Art] The equipment used as the dual structure of the quartz crucible for fusing silicon and the graphite crucible which contains this and is held from an outside is used for raising actuation of the silicon single crystal by the CZ process. and -- the time of performing this raising actuation -- a quartz crucible and a graphite crucible -- the elevated temperature near 1500 degree C -- contacting -- the silicifications mainly following between these two crucibles -- it is thought that a reaction and oxidative consumption advance.
$SiO_2+C \rightarrow SiO+CO$ -- (1)
$SiO+2\ C \rightarrow SiC+CO$ -- (2)
$SiC+2SiO_2 \rightarrow 3\ SiO+CO$ -- (3)
[0003] namely, the SiO gas generated in connection with the oxidative consumption of the graphite by the reaction formula (1) -- the inside of the pore inside a graphite organization -- being spread -- a reaction formula (2) -- a graphite -- SiC -- converting -- the interior of the inside front face of a graphite crucible to a crucible -- gradually -- silicification -- going on -- the surface part from the inside front face of a graphite crucible -- applying -- silicification -- a layer is formed. furthermore, this silicification -- in order to exhaust the graphite and SiC which are contained in a layer by the reaction formula (1) and (3) by contact to a quartz crucible, respectively, the phenomenon (the so-called "thinning") in which the thickness of a graphite crucible becomes thin advances. And generally, although the life of a graphite crucible is performed by judging the situation of thinning by oxidative consumption visually, it has the case where use of a crucible becomes impossible by cause except thinning by the above-mentioned oxidization consumption. It is the case where curvature and breakage arise in a graphite crucible, and specifically, the situation where it becomes impossible by the cause using this curvature and breakage happens, before a thinning phenomenon advances. For this reason, in order that such curvature and breakage may reduce the endurance of a graphite crucible and may shorten the life of a crucible remarkable, they are a problem more serious than the above-mentioned oxidative consumption.

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[0004] by the way -- if a graphite crucible is made into the structure of one apparatus -- silicification -- it has two division which generally carried out the vertical division of the graphite crucible perpendicularly, or trichotomized structure from the reason for being easy to produce breakage that it is easy to be influenced of distortion by the reaction, and in case a quartz crucible is held, between each divided part, it **********s inevitably and a part arises. Here, the graphite crucible of 2 block construction is adjusted each other compared with the thing of trichotomy structure, there are few parts, and the flow of the SiO gas in this adjustment part reduces it, and it has an advantage of the ability of thinning by oxidative consumption to reinforcement-make it hard to occur as a result. however -- the graphite crucible of these 2 block construction -- the thing of trichotomy structure -- comparing -- geometrical -- silicification -- the internal stress by the reaction increases and there is another problem of being easy to generate breakage etc., and it has been a serious failure, when this problem adopts 2 block construction and much more reinforcement is attained.

[0005] furthermore -- the silicon wafer manufacture field in recent years -- manufacture of the diameter silicon single crystal of macrostomia 8 inches or more -- in use -- becoming -- while -- this -- following -- the size of a graphite crucible -- enlargement -- needed -- silicification -- the internal distortion of the graphite crucible by the reaction tends to increase, and it is in the inclination which the degree of curvature and the frequency of breakage increase.

[0006] the curvature of this graphite crucible and the phenomenon of breakage are indicated by the publication-number No. 172887 [two to] official report -- as -- silicification of said reaction formula (2) -- the purpose which cubical expansion happens with a reaction, and distortion produced inside a graphite crucible in this case is considered to be the cause, and solves this problem -- it is -- silicification -- in order to control a reaction, the graphite crucible (JP,58-156595,A, JP,63-85086,A) which reduced the pore diameter or the gas transmittance of a graphite is proposed.

[0007]
[Problem(s) to be Solved by the Invention] However, if according to this invention persons' examination result generating of breakage etc. cannot necessarily be prevented in the graphite crucible which reduced the pore diameter etc. in this way but the pore diameter of graphite material is conversely made small the silicification which diffusion of the SiO gas inside a graphite organization is controlled, and is generated -- SiC in a layer -- eburnation -- carrying out -- silicification -- the coefficient of cubical expansion of a layer became high, and it became clear that it on the contrary became easy to generate the curvature of a graphite crucible and breakage.

[0008] then, the silicification generated as a result of this invention persons' inquiring wholeheartedly about the curvature of a graphite crucible, or the cause of breakage -- the SiC content in a layer -- generating of this curvature and breakage -- direct -- influencing -- **** -- this silicification -- it found out that the curvature of a graphite crucible and breakage could be prevented as much as possible by stopping the SiC content in a layer

low. and this silicification -- the average pore diameter and the rate of an open pore of graphite material which form a graphite crucible in order to make SiC content in a layer low -- the predetermined range -- carrying out -- silicification -- being able to attain by controlling a reaction and optimizing an elastic modulus further -- silicification -- distortion caused by the cubical expansion accompanying formation of a layer could be controlled, and it found out that the endurance of a graphite crucible was notably improvable as a result.

[0009] Therefore, the purpose of this invention mitigation-izes the curvature and breakage at the time of raising actuation of the silicon single crystal by the CZ process, and is to offer the graphite crucible excellent in endurance for silicon single crystal manufacture.

[0010]
[Means for Solving the Problem] That is, for this invention, the average pore diameter d measured by the method of mercury penetration is 3 micrometer<d <=7micrometer, and the rate of an open pore is 10 - 20%, and an elastic modulus is 2 800-1600kg/mm. It is the graphite crucible for silicon single crystal manufacture equipped with the property.

[0011] the silicification which SiO gas diffuses the average pore diameter of a graphite crucible, and the value of the rate of an open pore inside a graphite organization, and is reacted and generated in this invention -- the SiC content in a layer, and this silicification -- it is an indispensable matter in order to reduce the reactivity of a reaction.

[0012] this invention -- setting -- the average pore diameter d of a graphite crucible -- the range of 3 micrometer<d <=7micrometer -- it is necessary to make it preferably the range of 3 micrometer<d <=5micrometer Thus, by making the average pore diameter d of a graphite crucible into the range of 3 micrometer<d <=7micrometer the field inside a graphite crucible where SiO gas is deep -- being spread -- up to a field deep in the thickness direction of a graphite crucible peripheral wall -- silicification -- a layer -- forming -- this silicification, if the field of a layer becomes thick SiC content -- low -- becoming -- consequently, silicification -- the difference of the coefficient of cubical expansion between the graphite layers (layer which is not silicified) of a layer which are inside further becomes small, and a big distortion which causes the curvature of a graphite crucible and breakage by this is not produced, either.

[0013] the silicification which the SiO gas which a hot quartz crucible and a hot graphite crucible contact, and occurs could not be diffused even from the inside front face of a graphite crucible to the deep field of a graphite in-house, but generated SiC only in the shallow field of a graphite crucible surface, and was formed in this shallow field here when the average pore diameter d of a graphite crucible was 3 micrometers or less -- the SiC content of a layer rises. the silicification which is high compared with a graphite as for the coefficient of cubical expansion of SiC, and contains this SiC here -- the coefficient of cubical expansion of a layer -- SiC content -- it is proportional -- high -- becoming -- this silicification -- the difference of the coefficient of cubical expansion between the graphite layers which adjoin inside a layer becomes large, for this reason it

becomes easy to generate curvature and breakage in a graphite crucible. the useful effectiveness by decline in the SiC content by diffusion of SiO gas if the average pore diameter d of a graphite crucible exceeds 7 micrometers on the contrary, or decline in the coefficient of cubical expansion accompanying this – silicification -- the direction of the bad influence by the fall of that the reaction surface area which participates in a reaction increases, or a mechanical strength serves as size.

[0014] this invention -- setting -- the rate of an open pore of a graphite crucible -- 10 - 20% of range -- it is necessary to be 10 - 16% of range preferably Reaction surface area increases. since the rate of an open pore of this graphite crucible influences reaction surface area -- silicification, if reacting weight and the amount of oxidative consumption are influenced and it exceeds 20% even if an average pore diameter is above-mentioned within the limits -- silicification -- breakage being caused, and a life becoming short, without the ability reducing SiC content in a layer, and that it is less than 10% on the contrary the time of baking -- setting -- molding -- the cracked gas which occurs from a binder component in the living body -- escaping -- hard -- a crack -- occurring -- being easy -- the product yield at the time of manufacturing a large-sized graphite crucible falls, and also the graphite crucible of the quality-of-the-material property that an average pore diameter exceeds 3 micrometers becomes difficult to get, and it becomes easy to damage it. In addition, the rate of an open pore of this graphite crucible is measuring the volume of the mercury which permeated by the pressure to 60000Psia(s) to the graphite crucible with a method of mercury penetration, and is a value defined as a rate of the volume of the seepage water silver content to a graphite crucible.

[0015] this invention -- setting -- silicification -- the SiC content contained in a layer can be measured by carrying out Rhine analysis of the reaction layer cross section of a graphite crucible by EPMA (X-ray microanalyser). Reacting weight is large, the curvature starting position in the wall inside SiC content can take maximum of the measurement part of this SiC content, i.e., the location where it applies to a bottom wall from the side attachment wall of a graphite crucible, and curvature begins to be attached, is good, and the SiC content measured in this part often reflects the effect of breakage etc. the SiC content measured by EPMA -- silicification -- there is an inclination which decreases from a layer front face although it is small as it becomes deep in the direction of the interior. therefore, the silicification about this invention -- the SiC content contained in a layer -- silicification -- a layer -- the field of the width of face of the micron unit of specification [the thickness direction] -- dividing -- the SiC content (% of the weight) for every field -- asking -- these -- averaging -- silicification -- it is the value calculated as the average of the whole layer.

[0016] the silicification formed in the graphite crucible by this invention -- SiC content contained in a layer can be made 40% or less, and the curvature of a graphite crucible and breakage can be effectively controlled also in manufacture of a silicon single crystal 8 inches or more. On the other hand, in that by which SiC content exceeds 40%, curvature and breakage become what has a short endurance life that it is easy to generate in few use counts.

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[0017] the silicification formed during raising actuation of a silicon single crystal at a graphite crucible -- the depth of a layer -- usually -- the range of about 1-3mm -- it is -- case the rate of an open pore of a graphite crucible is comparable -- silicification -- if a layer is deep -- the SiC content within a layer -- small -- reverse -- silicification -- if a reaction layer is shallow, SiC content will become greatly that it is easy to carry out eburnation of the SiC within a layer. Here, a graphite crucible with the former small SiC content can make low stress generated inside, and it can control curvature and breakage. therefore, silicification -- a layer -- the depth -- breakage of a graphite crucible -- a problem -- not becoming -- silicification -- the size of the SiC content in a layer does effect greatly.

[0018] this invention -- setting -- the elastic modulus of a graphite crucible -- 800-1600kg/mm2 -- desirable -- 1000-1300kg/mm2 ** -- it is necessary to carry out the value measured by the resonance method with which the elastic modulus of this graphite crucible applied to JIS-R7202 correspondingly -- it is -- silicification -- the silicification which carried out cubical expansion by the reaction -- when a layer makes a graphite crucible produce distortion, the magnitude of the stress generated in this graphite crucible is determined. here -- an elastic modulus -- 800kg/mm2 the following -- silicification -- in order to ease distortion by the cubical expansion of a layer, a graphite crucible deforms easily, and it becomes impossible to stabilize for it and support the quartz crucible held inside, and it has a bad influence on manufacture of a silicon single crystal. opposite -- an elastic modulus -- 1600kg/mm2 if it exceeds -- silicification -- relaxation of the stress by deformation of a graphite crucible cannot break out easily to distortion by the cubical expansion of a layer, the absolute value of the stress generated inside a graphite crucible becomes large, and it becomes easy to produce breakage.

[0019] What is necessary is to be carrying out particle size of a raw material coke breeze to ** greatly manufacturing the graphite crucible in this invention, and just to control the grain size of this raw material coke breeze in the predetermined range, in order to manufacture the graphite crucible which has a specific average pore diameter, since the average pore diameter of a graphite crucible is expanded. And since it is dependent on contraction of the molding object of the time of baking, the rate of an open pore of a graphite crucible can acquire the rate value of an open pore made into the purpose by optimizing the heat kneading conditions of coke breezes, such as an appending rate of a binder, and a binder in addition to the particle size of a raw material coke breeze. Moreover, in order to influence the elastic modulus of a graphite crucible of graphitization temperature in addition to the aforementioned conditions, it acquires the elastic-modulus value made into the purpose by processing at the temperature of the range of 2000-3000 degrees C.

[0020]
[Embodiment of the Invention] Hereafter, the graphite crucible of this invention is explained in accordance with the gestalt of operation. The graphite crucible in this invention can manufacture the secondary powder which pulverized the kneading object of a fines-like coke breeze and binders, such as a tar pitch, by calcinating and

graphitization processing after molding by the rubber press. And it is the average pore diameter d of the range of 3 micrometer<d <=7micrometer, the rate of an open pore of 10 - 20% of range, and 800-1600kg/mm2 by making the grain size of a coke breeze, a binder appending rate, graphitization temperature, etc. into a suitable value, and manufacturing them. The graphite crucible which has the modulus of elasticity of the range can be manufactured. In addition, the graphite crucible of this operation gestalt can also be made into the structure which can also make it the structure of 2 division which distortion tends to generate, and is divided into two or more parts beyond trichotomy or it.

[0021] the silicification which a graphite crucible is contacting a quartz crucible at an elevated temperature in the manufacture process of a silicon single crystal, and contained SiC in the inside of a graphite crucible -- a layer is formed. this silicification -- the reaction accompanied by cubical expansion in a reaction -- it is -- silicification -- distortion arises inside a graphite crucible because a reaction layer carries out cubical expansion, breakage is caused, and a life becomes short.

[0022] the SiO gas which occurs in this invention in case a quartz crucible and a graphite crucible contact at an elevated temperature since the average pore diameter d of the graphite crucible measured with the method of mercury penetration is the magnitude which is 3 micrometer<d <=7micrometer -- the interior from the front face of a graphite crucible -- being spread -- silicification -- the result to which the thickness of a layer becomes large -- silicification -- the SiC content as the whole layer is stopped low. since [moreover,] the rate of an open pore is the range which is 10 - 20% -- silicification -- the amount of the SiC itself which can fall and generates the reaction itself can be reduced. therefore, the thing for which these average pore diameter and the rate of an open pore are made into the range of this invention -- consequent -- silicification -- the SiC content in a layer -- it can fall -- the result -- silicification -- the coefficient of cubical expansion of a layer can be reduction-ized, and the curvature of a graphite crucible and generating of breakage can be prevented. Moreover, it is the modulus of elasticity of a graphite crucible 800-1600kg/mm 2 The stress by distortion produced inside the graphite crucible is made to make it low by carrying out. therefore, a graphite crucible -- silicification -- the phenomenon which a layer is formed and curvature and breakage generate is prevented effectively.

[0023]
[Example] Next, based on examples 1-4 and the examples 1-5 of a comparison, this invention is explained concretely. The physical-properties value of the graphite crucible used in this example and the example of a comparison is as being shown in Table 1. These graphite crucibles are manufactured as a graphite crucible equipped with each physical properties, such as an average pore diameter value shown in Table 1, a rate value of an open pore, and a modulus-of-elasticity value, by adjusting suitably terms and conditions, such as heat kneading conditions of coke breezes, such as grain size of raw material corks, and an appending rate of a binder, and a binder, and graphitization temperature.

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[0024] From the high-purity-graphite material (10 ppm or less of ash content) from which a characteristic value differs, it set in silicon single crystal raising equipment using the graphite crucible for silicon single crystal manufacture of 2 division for the diameter of 24 inches, and the service test was performed.

[0025] the 1st table -- the durability test result of a graphite crucible -- uniting -- silicification -- the SiC content of the depth of a reaction and the average included in the layer was shown. here -- silicification -- the SiC content (beam diameter of 10 micrometers) which the SiC content within a layer carried out Rhine analysis of the cutting plane in the curvature starting position in the wall inside of a graphite crucible in the depth direction by EPMA (X-ray microanalyser), and was equalized by 100-micrometer width of face -- silicification -- it considered as the value averaged in all the fields of a layer. moreover, silicification -- the layer depth was made into the range where the SiC content in 100-micrometer width-of-face field by EPMA measurement is detected to 5% or more.

[0026] 75 use or more was more possible than the result of the 1st table in the condition that there is all no breakage in the examples 1-4 using the graphite crucible of this invention as low [SiC content] as 35% or less. Here, the thickness of the curvature starting position in the adjustment part of the graphite crucible exhausted most, i.e., the wall inside of a graphite crucible, judges the cause of a life by consumption as a time of decreasing to 70%.

[0027] on the other hand -- the examples 3 and 4 of a comparison in which less than 10% of the examples 1 and 2 of a comparison and the rate of an open pore exceed [an average pore diameter / 3 micrometers or less and the rate of an open pore] 20% -- silicification -- 45% or more of precise SiC layer was formed, and the SiC content contained in a layer was damaged with the small use count compared with the example. In the example 4 of a comparison which separates especially from all the requirements for a property of this invention, breakage arose in 15 times with extremely few use counts. moreover, an elastic modulus -- 1600kg/mm2 although SiC content was reduced to 36% in the example 5 of a comparison which exceeds -- silicification -- even if it was a slight distortion by the layer, it was thought that the stress generated in a graphite crucible became large, and breakage arose by 30 use.

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Table 1

例No.	平均気孔径 (μm)	開気孔率 (vol.%)	強性率 (kg/mm²)	ケイ化層深さ (μm)	SiC含有率 (wt.%)	耐用回数	寿命原因
実施例1	3.2	10	1550	1800	35	80	消耗
実施例2	4.5	15	1300	2000	35	82	消耗
実施例3	5.7	17	1100	2000	32	80	消耗
実施例4	7.0	20	850	2200	28	75	消耗
比較例1	0.5	8	1350	1000	63	30	破損
比較例2	2.9	14	1200	1300	45	35	破損
比較例3	4.2	21	1000	1700	55	40	破損
比較例4	7.6	23	770	1900	52	15	破損
比較例5	2.0	12	1620	1700	36	30	破損

[0028]
[Effect of the Invention] using the graphite crucible of this invention, as explained above -- silicification -- the SiC content in a reaction layer can be reduced and the graphite crucible for silicon single crystal manufacture which is excellent in the endurance which controlled the breakage at the time of raising actuation of the silicon single crystal by the CZ process can be offered by easing distortion produced inside a graphite crucible. By this, it is stabilized for a long time, raising of a silicon single crystal can be performed, and very remarkable effectiveness is brought about on [, such as reduction of a manufacturing cost,] industry.

[Translation done.]